

Variation of Parameters in Becke-3 Hybrid Exchange-Correlation Functional

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Received 8 June 1999; accepted 1 October 1999

ABSTRACT: We have investigated the consequences of varying the three parameters in Becke's hybrid exchange-correlation functional, which includes five contributions: Hartree–Fock exchange, local exchange, Becke's gradient exchange correction, local correlation, and some form of gradient correlation correction. Our primary focus was upon obtaining orbital energies with magnitudes that are reasonable approximations to the electronic ionization potentials; however, we also looked at the effects on molecular geometries and atomization enthalpies. A total of 12 parameter combinations was considered for each of three different gradient correlation corrections: the Lee–Yang–Parr, the Perdew-86, and the Perdew–Wang 91. Five molecules were included in the study: HCN, N₂, N₂O, F₂O, and H₂O. For comparison, a Hartree–Fock calculation was also carried out for each of these. The 6-31+G** basis set was used throughout this work. We found that the ionization potential estimates can be greatly improved (to much better than Hartree–Fock levels) by increasing the Hartree–Fock exchange contribution at the expense of local exchange. In itself, this also introduces major errors in the atomization enthalpies. However, this can be largely or even completely counteracted by reducing or eliminating the role of the gradient exchange correction. © 2000 John Wiley & Sons, Inc. *J Comput Chem* 21: 227–238, 2000

Keywords: Becke three-parameter hybrid functional; ionization potentials; Kohn–Sham orbital energies

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Contract/grant sponsor: Office of Naval Research; contract/grant number: N00014-99-1-0393

Introduction

The Kohn–Sham version of density functional theory is in principle exact for the ground-state electron density and total energy.^{1–3} In practice, however, it requires an approximation to the exchange–correlation functional. A number of these have been proposed in recent years, and several are encoded in the Gaussian 94⁴ and Gaussian 98⁵ systems of programs. Particularly widely used is Becke’s three-parameter hybrid functional (B3⁶), which combines, in variable proportions, local and nonlocal treatments of exchange and correlation with Hartree–Fock exchange. (Gaussian 98 also offers Becke’s recent one-parameter expression;⁷ however, our present interest is in the earlier, more flexible one.)

As implemented in Gaussian 94 and Gaussian 98,^{4,5} Becke’s three parameter hybrid has the form,

$$E_{xc} = \alpha E_x^{\text{Slater}} + (1 - \alpha) E_x^{\text{HF}} + \beta \Delta E_x^{\text{Becke}} + E_c^{\text{VWN}} + \gamma \Delta E_c^{\text{nonlocal}} \quad (1)$$

The exchange energy is written as a sum of Hartree–Fock (HF) and local (Slater⁸) contributions plus Becke’s gradient correction;⁹ the correlation energy is given by a local Vosko–Wilk–Nusair formula (VWN III, based on the RPA uniform electron gas¹⁰), supplemented by some form of nonlocal (gradient) correction. The possibilities for the latter are those in the Lee–Yang–Parr (LYP¹¹), the Perdew–86 (P86¹²), and the Perdew–Wang 91 (PW91¹³) functionals.

Becke determined the values of the parameters α , β , and γ by a linear least-squares fit to 56 atomization energies, 42 ionization potentials, 8 proton affinities, and 10 atomic energies,⁶ taken from the G1 database.^{14,15} Using the Perdew–Wang gradient correction and their electron-gas parametrization for the local term in eq. (1), he obtained $\alpha = 0.80$, $\beta = 0.72$, and $\gamma = 0.81$. Gaussian 94 and Gaussian 98 employ these values of α , β , and γ for the LYP and P86 nonlocal corrections, as well as the PW91, and introduce the VWN III for the local contribution.

These B3 procedures (B3LYP, B3PW91, and B3P86) have been overall quite successful.^{16–21} For example, the average absolute error in 28 B3P86/6-31+G(d,p) dissociation energies was 1.9 kcal/mol,¹⁹ and in 148 B3LYP/6-311+G(3df,2p) enthalpies of formation, 3.11 kcal/mol.¹⁶ For molecules containing third-row atoms, the average absolute error in B3PW91/6-311+G(3df,2p) atomization energies,

ionization potentials, electron affinities and proton affinities was 2.03 kcal/mol.¹⁸

Nevertheless, it is interesting to consider the possibility of improving the results for a particular property or class of molecules by appropriately changing the values of α , β , and γ in eq. (1), an option that is available in both Gaussian 94 and Gaussian 98.^{4,5} For example, the poor descriptions of Cr₂ that have been obtained with eq. (1) have led to suggestions that it be reparametrized in terms of a database that includes molecules containing transition metal atoms.^{22,23}

A property that might usefully be the target of reparametrization are the orbital energies, ε_i . The interpretation of these continues to be the focus of considerable attention.^{24–37} It is tempting to view their magnitudes as approximations to electronic ionization potentials, I_i , as is frequently done for their Hartree–Fock counterparts; however, the B3 values differ by greater amounts from the experimental data, typically being too low by at least 2 eV and often much more.³⁴ For a given exchange–correlation functional, however, the differences tend to be roughly similar, even for different molecules. (This is not the case at the Hartree–Fock level.³⁴) Thus, B3 orbital energies can be quite satisfactory for applications that depend upon trends in ionization potentials.^{35,36}

Our objective in this work has been to find a set or sets of parameters α , β , and γ for eq. (1) that produce $|\varepsilon_i|$ that are in good agreement with measured electronic ionization potentials. We assess possible negative consequences for other molecular properties by comparing the various calculated geometries and atomization enthalpies with experimental data. Because atomization energies were one of the properties originally used by Becke to determine the parameters,⁶ any change in the latter can be expected to produce poorer results for the former. It is the degree that will be of interest.

Procedure

We computed optimized geometries and energies for five different molecules, using the LYP, PW91, and P86 correlation corrections and various combinations of selected α , β , and γ values in eq. (1). Because it has been shown that actual electronic ionization potentials lie between the B3 and the Hartree–Fock $|\varepsilon_i|$,^{26,34} an obvious first step was to increase the contribution of the Hartree–Fock exchange in eq. (1), i.e., decrease α , which we did in several stages, going from $\alpha = 0.80$ to $\alpha =$

0.30 while keeping β and γ constant. By eq. (1), this simultaneously diminishes the role of Slater's local exchange term. For $\alpha = 0.40$, we also incrementally reduced Becke's nonlocal exchange. As a limiting case, we eliminated both local and nonlocal exchange, and kept only the Hartree–Fock ($\alpha = \beta = 0$). We also assessed the effect of correlation, by both increasing and decreasing γ . For comparison purposes, we carried out a Hartree–Fock calculation for each molecule. The 6-31+G** basis set and Gaussian 94⁴ were used throughout this work.

For each α , β , γ combination, we computed ΔH (298 K) for the separation of the molecule into its ground-state atoms. We have shown earlier that the zero-point plus thermal corrections in going from E_{\min} (0 K) to H (298 K) are very nearly the same for the B3LYP, B3PW91, and B3P86 functionals, for several different basis sets.³⁸ We found now that the consequences of changing the parameters are somewhat greater, but usually not more than about 1 kcal/mol, and often much less. Because our purpose in calculating the enthalpies of atomization is simply to monitor the effects of varying the parameters, we used an average value for the correction term for each molecule, rather than computing it separately for each of the total of 180 cases considered. The resulting error should generally be less than 0.5 kcal/mol.

Results

The molecules included in this study are HCN, N₂, N₂O, F₂O, and H₂O. Our results are presented in Tables I–V. Each table includes the optimized geometries and total energies, the B3 $|\varepsilon_i|$ and the enthalpies of atomization at 298 K obtained for a given molecule using the LYP, PW91, and P86 correlation corrections and 12 different α , β , γ combinations. Experimental and Hartree–Fock values are also given. The $|\varepsilon_i|$ are to be compared to measured vertical ionization potentials determined by means of photoelectron spectroscopy,³⁹ the level of agreement being indicated by the root-mean-square (rms) error.

For each functional, the first α , β , γ set is the standard one used in Gaussian 94 and Gaussian 98: $\alpha = 0.80$, $\beta = 0.72$, $\gamma = 0.81$. The next eight α , β , γ combinations explore various treatments of exchange. First, α is decreased incrementally to 0.30, holding β and γ constant. This gradually increases the Hartree–Fock contribution at the expense of the local (Slater). Next, the effect of reducing the nonlocal (Becke) exchange is examined, by setting β

to 0.50, 0.25, and 0.00 (with $\alpha = 0.40$, $\gamma = 0.81$). This is followed by eliminating both the local and nonlocal terms ($\alpha = \beta = 0$) and keeping only Hartree–Fock exchange. (Some of the calculations for N₂ and F₂O produce orbital orderings that differ from the experimental; this is consistently observed for the Hartree–Fock and the B3 with $\alpha = \beta = 0$.) Finally, the last three α , β , γ combinations investigate the consequences of both increasing and decreasing the role of nonlocal correlation ($\gamma = 1.00$ and $\gamma = 0.60$, respectively). The results for the various properties will be summarized in turn.

IONIZATION POTENTIALS

Confirming earlier findings,³⁴ the experimental ionization potentials are overestimated by the Hartree–Fock $|\varepsilon_i|$ (rms errors between 1.26 and 2.75 eV) and underestimated by the B3 with standard α , β , γ (rms errors between 2.49 and 3.91 eV). As expected, however, the B3 $|\varepsilon_i|$ can be increased dramatically by enlarging the Hartree–Fock exchange contribution, i.e., reducing α while holding β and γ constant. Already for $\alpha = 0.40$, the rms errors are less than 1.00 eV for all three correlation functionals (LYP, PW91, and P86), and they range as low as 0.18 eV (for H₂O, P86). On the other hand, the combination of only Hartree–Fock exchange with local and nonlocal correlation ($\alpha = \beta = 0$) is not desirable in the present context; the $|\varepsilon_i|$ and the rms errors actually become considerably higher than the Hartree–Fock values. Decreasing the nonlocal exchange correction (by reducing β) and modifying the extent of nonlocal correlation (via γ) have variable but usually relatively small effects upon the rms error, although there are some exceptions.

GEOMETRIES

The bond lengths all show basically the same pattern, and the results are usually similar for the LYP, PW91, and P86 calculations (except for the N—O and F—O bonds, for which the LYP distances are consistently somewhat longer). The Hartree–Fock tend to be too short; as anticipated, this is largely remedied by the introduction of correlation,⁴³ so that the B3 with standard hybrid parameters ($\alpha = 0.80$, $\beta = 0.72$, $\gamma = 0.81$) are quite accurate. Increasing the role of Hartree–Fock exchange by reducing α progressively shortens the bonds, most markedly in F₂O, and in the limit of no density functional exchange ($\alpha = \beta = 0$), they are actually worse than the pure Hartree–Fock. Varying the contributions of nonlocal exchange and correlation (by changing β

TABLE I.
Experimental and Computed Data for HCN.

Method ^a	Distances, Å		<i>I</i> _j or <i>ε</i> _j , ev			rms error, ev	<i>E</i> _{tot} , hartrees	Δ <i>H</i> _{atomiz.} , kcal/mol
	H—C	C—N						
Experiment ^b	1.065	1.153	13.80	14.15	19.68	—	—	304.1
Hartree–Fock	1.060	1.133	13.70	15.80	22.14	1.71	−92.88066	187
B3LYP:								
0.80, 0.72, 0.81	1.071	1.158	10.10	10.70	16.78	3.37	−93.43061	300
0.60, 0.72, 0.81	1.063	1.148	11.28	12.28	18.50	1.94	−93.66497	280
0.50, 0.72, 0.81	1.059	1.144	11.88	13.08	19.37	1.28	−93.78295	271
0.40, 0.72, 0.81	1.055	1.140	12.48	13.89	20.24	0.84	−93.90144	262
0.30, 0.72, 0.81	1.052	1.136	13.08	14.70	21.12	0.98	−94.02043	252
0.40, 0.50, 0.81	1.058	1.139	12.46	13.79	20.10	0.84	−93.62756	272
0.40, 0.25, 0.81	1.061	1.139	12.45	13.69	19.94	0.84	−93.31669	283
0.40, 0.00, 0.81	1.064	1.138	12.43	13.58	19.78	0.86	−93.00619	295
0.00, 0.00, 0.81	1.051	1.124	14.85	16.85	23.26	2.66	−93.48260	259
0.40, 0.72, 1.00	1.056	1.141	12.29	13.70	20.04	0.93	−93.76413	261
0.30, 0.72, 1.00	1.053	1.137	12.89	14.51	20.91	0.91	−93.88306	252
0.30, 0.72, 0.60	1.050	1.135	13.28	14.91	21.36	1.11	−94.17230	253
B3PW91:								
0.80, 0.72, 0.81	1.071	1.157	10.13	10.68	16.78	3.36	−93.38740	298
0.60, 0.72, 0.81	1.063	1.148	11.33	12.26	18.51	1.92	−93.62217	279
0.50, 0.72, 0.81	1.060	1.144	11.93	13.06	19.37	1.26	−93.74034	269
0.40, 0.72, 0.81	1.056	1.140	12.53	13.87	20.25	0.82	−93.85902	260
0.30, 0.72, 0.81	1.052	1.136	13.14	14.69	21.13	0.97	−93.97819	251
0.40, 0.50, 0.81	1.059	1.139	12.52	13.78	20.10	0.81	−93.58515	270
0.40, 0.25, 0.81	1.061	1.139	12.50	13.68	19.94	0.81	−93.27428	282
0.40, 0.00, 0.81	1.064	1.138	12.49	13.57	19.78	0.83	−92.96379	293
0.00, 0.00, 0.81	1.052	1.124	14.92	16.84	23.27	2.67	−93.44089	258
0.40, 0.72, 1.00	1.057	1.140	12.48	13.80	20.16	0.84	−93.77647	261
0.30, 0.72, 1.00	1.053	1.136	13.09	14.61	21.04	0.92	−93.89564	252
0.30, 0.72, 0.60	1.051	1.136	13.20	14.77	21.23	1.02	−94.06947	250
B3P86:								
0.80, 0.72, 0.81	1.071	1.157	10.70	11.25	17.35	2.80	−93.67108	308
0.60, 0.72, 0.81	1.063	1.148	11.89	12.83	19.07	1.39	−93.90594	288
0.50, 0.72, 0.81	1.059	1.143	12.49	13.64	19.94	0.83	−94.02416	279
0.40, 0.72, 0.81	1.055	1.139	13.10	14.44	20.82	0.79	−94.14288	270
0.30, 0.72, 0.81	1.052	1.135	13.70	15.26	21.70	1.33	−94.26210	261
0.40, 0.50, 0.81	1.058	1.139	13.08	14.35	20.67	0.72	−93.86901	280
0.40, 0.25, 0.81	1.061	1.138	13.07	14.25	20.51	0.64	−93.55814	291
0.40, 0.00, 0.81	1.064	1.138	13.05	14.14	20.35	0.58	−93.24764	303
0.00, 0.00, 0.81	1.051	1.123	15.48	17.41	23.84	3.20	−93.72490	267
0.40, 0.72, 1.00	1.057	1.140	13.06	14.38	20.74	0.76	−94.06221	271
0.30, 0.72, 1.00	1.053	1.136	13.66	15.20	21.62	1.28	−94.18143	262
0.30, 0.72, 0.60	1.051	1.135	13.74	15.32	21.78	1.39	−94.35131	259

^a All calculations were with the 6-31+G** basis set. For each functional combination, the values of A, B, and C are given to identify the parametrization. The first set (A = 0.80, B = 0.72, and C = 0.81) is the standard one.

^b Distances: ref. 39; ionization potentials: ref. 40; atomization energies: ref. 41.

TABLE II.
Experimental and Computed Data for N₂.

Method ^a	Distances, Å	I_i or $ \varepsilon_i $, eV			rms error, eV	E_{tot} , hartrees	$\Delta H_{\text{atomiz.}}$, kcal/mol
Experiment ^b	1.098	15.60	16.98	18.78	—	—	226.0
Hartree–Fock	1.078	17.31	17.02	21.08	1.65	−108.94702	106
B3LYP:							
0.80, 0.72, 0.81	1.105	11.95	12.87	15.35	3.74	−109.52978	220
0.60, 0.72, 0.81	1.096	13.61	14.20	17.12	2.19	−109.77762	200
0.50, 0.72, 0.81	1.091	14.45	14.87	18.01	1.46	−109.90230	190
0.40, 0.72, 0.81	1.087	15.30	15.54	18.91	0.85	−110.02746	181
0.30, 0.72, 0.81	1.083	16.15	16.21	19.80	0.80	−110.15310	171
0.40, 0.50, 0.81	1.086	15.21	15.54	18.78	0.86	−109.73372	188
0.40, 0.25, 0.81	1.085	15.12	15.54	18.65	0.88	−109.40017	197
0.40, 0.00, 0.81	1.085	15.02	15.54	18.51	0.91	−109.06690	205
0.00, 0.00, 0.81	1.070	18.44	18.23	22.11	2.63	−109.57060	169
0.40, 0.72, 1.00	1.088	15.10	15.36	18.71	0.98	−109.88749	181
0.30, 0.72, 1.00	1.084	15.95	16.03	19.61	0.76	−110.01308	171
0.30, 0.72, 0.60	1.083	16.37	16.42	20.02	0.90	−110.30789	171
B3PW91:							
0.80, 0.72, 0.81	1.104	11.90	12.91	15.37	3.74	−109.48157	216
0.60, 0.72, 0.81	1.095	13.56	14.25	17.15	2.18	−109.72987	196
0.50, 0.72, 0.81	1.091	14.40	14.93	18.04	1.44	−109.85477	187
0.40, 0.72, 0.81	1.086	15.25	15.60	18.94	0.83	−109.98015	177
0.30, 0.72, 0.81	1.083	16.10	16.28	19.84	0.79	−110.10598	168
0.40, 0.50, 0.81	1.086	15.17	15.60	18.82	0.83	−109.68641	185
0.40, 0.25, 0.81	1.085	15.07	15.60	18.68	0.86	−109.35288	193
0.40, 0.00, 0.81	1.084	14.98	15.60	18.55	0.88	−109.01962	202
0.00, 0.00, 0.81	1.070	18.40	18.31	22.15	2.64	−109.52408	166
0.40, 0.72, 1.00	1.086	15.16	15.55	18.87	0.87	−109.89444	178
0.30, 0.72, 1.00	1.083	16.02	16.23	19.77	0.76	−110.02030	169
0.30, 0.72, 0.60	1.082	16.20	16.34	19.92	0.83	−110.20071	167
B3P86:							
0.80, 0.72, 0.81	1.104	12.48	13.49	15.95	3.16	−109.76926	224
0.60, 0.72, 0.81	1.094	14.14	14.83	17.72	1.62	−110.01765	204
0.50, 0.72, 0.81	1.090	14.98	15.50	18.62	0.93	−110.14258	195
0.40, 0.72, 0.81	1.086	15.83	16.18	19.52	0.64	−110.26800	185
0.30, 0.72, 0.81	1.082	16.69	16.85	20.42	1.14	−110.39387	176
0.40, 0.50, 0.81	1.085	15.75	16.18	19.39	0.59	−109.97426	193
0.40, 0.25, 0.81	1.084	15.65	16.17	19.26	0.54	−109.64072	201
0.40, 0.00, 0.81	1.083	15.56	16.17	19.12	0.51	−109.30745	210
0.00, 0.00, 0.81	1.069	18.98	18.88	22.73	3.20	−109.81206	174
0.40, 0.72, 1.00	1.086	15.76	16.14	19.46	0.63	−110.18445	186
0.30, 0.72, 1.00	1.082	16.62	16.81	20.36	1.09	−110.31034	177
0.30, 0.72, 0.60	1.082	16.76	16.89	20.48	1.19	−110.48624	175

^a All calculations were with the 6-31+G** basis set. For each functional combination, the values of A, B, and C are given to identify the parametrization. The first set (A = 0.80, B = 0.72, and C = 0.81) is the standard one.

^b Distances: ref. 39; ionization potentials: ref. 40; atomization energies: ref. 41.

TABLE III.
Experimental and Computed Data for N₂O.

Method ^a	Distances, Å		<i>I</i> _i or ϵ_i , ev				rms error, ev	<i>E</i> _{tot} , hartrees	$\Delta H_{\text{atomiz.}}$, kcal/mol
	N—N	N—O							
Experiment ^b	1.128	1.184	12.89	16.38	18.23	20.11	—	—	266.0
Hartree–Fock	1.091	1.181	13.54	19.05	21.15	22.51	2.34	−183.68528	73
B3LYP:									
0.80, 0.72, 0.81	1.133	1.195	9.64	13.32	15.56	16.75	3.10	−184.66830	261
0.60, 0.72, 0.81	1.119	1.189	10.88	15.08	17.29	18.51	1.51	−185.04660	220
0.50, 0.72, 0.81	1.112	1.187	11.52	15.97	18.14	19.39	0.80	−185.23746	200
0.40, 0.72, 0.81	1.106	1.186	12.16	16.87	18.99	20.28	0.59	−185.42940	181
0.30, 0.72, 0.81	1.100	1.185	12.82	17.78	19.84	21.16	1.19	−185.62239	162
0.40, 0.50, 0.81	1.106	1.181	12.12	16.76	19.03	20.21	0.59	−184.96728	198
0.40, 0.25, 0.81	1.105	1.175	12.08	16.64	19.08	20.14	0.60	−184.44267	218
0.40, 0.00, 0.81	1.104	1.171	12.04	16.51	19.12	20.07	0.62	−183.91859	238
0.00, 0.00, 0.81	1.083	1.166	14.69	20.15	22.49	23.66	3.47	−184.69391	165
0.40, 0.72, 1.00	1.107	1.186	11.97	16.67	18.81	20.08	0.56	−185.20893	182
0.30, 0.72, 1.00	1.101	1.185	12.63	17.58	19.65	20.97	1.03	−185.40185	163
0.30, 0.72, 0.60	1.100	1.185	13.03	18.00	20.05	21.38	1.38	−185.86620	161
B3PW91:									
0.80, 0.72, 0.81	1.132	1.189	9.65	13.30	15.65	16.80	3.07	−184.59574	262
0.60, 0.72, 0.81	1.118	1.183	10.89	15.05	17.39	18.57	1.49	−184.97495	221
0.50, 0.72, 0.81	1.112	1.181	11.53	15.94	18.25	19.46	0.79	−185.16622	201
0.40, 0.72, 0.81	1.106	1.179	12.18	16.84	19.10	20.35	0.62	−185.35855	182
0.30, 0.72, 0.81	1.100	1.178	12.84	17.75	19.95	21.25	1.24	−185.55191	162
0.40, 0.50, 0.81	1.105	1.175	12.14	16.73	19.14	20.29	0.62	−184.89658	199
0.40, 0.25, 0.81	1.104	1.170	12.10	16.61	19.18	20.22	0.63	−184.37212	219
0.40, 0.00, 0.81	1.104	1.165	12.06	16.49	19.22	20.15	0.65	−183.84819	239
0.00, 0.00, 0.81	1.083	1.160	14.71	20.12	22.62	23.77	3.53	−184.62487	166
0.40, 0.72, 1.00	1.106	1.177	12.11	16.76	19.06	20.30	0.61	−185.22492	185
0.30, 0.72, 1.00	1.100	1.176	12.77	17.66	19.92	21.20	1.19	−185.41831	166
0.30, 0.72, 0.60	1.100	1.180	12.91	17.84	20.00	21.31	1.29	−185.69962	159
B3P86:									
0.80, 0.72, 0.81	1.131	1.188	10.23	13.88	16.23	17.38	2.49	−185.05242	274
0.60, 0.72, 0.81	1.118	1.182	11.47	15.63	17.97	19.15	0.94	−185.43175	233
0.50, 0.72, 0.81	1.111	1.180	12.11	16.52	18.83	20.04	0.50	−185.62307	213
0.40, 0.72, 0.81	1.105	1.179	12.76	17.42	19.69	20.94	0.99	−185.81545	193
0.30, 0.72, 0.81	1.099	1.178	13.41	18.33	20.54	21.83	1.76	−186.00885	174
0.40, 0.50, 0.81	1.105	1.174	12.72	17.32	19.72	20.87	0.96	−185.35347	211
0.40, 0.25, 0.81	1.104	1.170	12.68	17.19	19.76	20.80	0.94	−184.82901	231
0.40, 0.00, 0.81	1.103	1.165	12.63	17.07	19.80	20.73	0.92	−184.30507	251
0.00, 0.00, 0.81	1.083	1.160	15.29	20.70	23.20	24.35	4.10	−185.08193	178
0.40, 0.72, 1.00	1.106	1.177	12.71	17.36	19.66	20.90	0.96	−185.68558	197
0.30, 0.72, 1.00	1.100	1.176	13.36	18.26	20.51	21.80	1.72	−185.87901	178
0.30, 0.72, 0.60	1.099	1.179	13.47	18.41	20.56	21.87	1.80	−186.15243	170

^a All calculations were with the 6-31+G** basis set. For each functional combination, the values of A, B, and C are given to identify the parametrization. The first set (A = 0.80, B = 0.72, and C = 0.81) is the standard one.

^b Distances: ref. 39; ionization potentials: ref. 40; atomization energies: ref. 41.

TABLE IV.
Experimental and Computed Data for OF₂.

Method ^a	Distance, Å	Angle, deg.	I_i or $ \varepsilon_i $, ev							rms error, ev	E_{tot} , hartrees	$\Delta H_{\text{atomiz.}}$, kcal/mol
Experiment ^b	1.412	103.2	13.26	16.17	16.32	16.47	18.68	19.50	20.90	—	—	91.7
Hartree-Fock	1.3477	103.3	15.42	17.91	18.63	19.87	22.96	22.55	22.54	2.80	-273.46365	-44
B3LYP:												
0.80, 0.72, 0.81	1.413	104.0	9.74	12.69	12.53	12.99	15.30	15.99	17.26	3.55	-274.67284	88
0.60, 0.72, 0.81	1.395	103.6	11.53	14.34	14.37	15.03	17.52	17.82	18.80	1.72	-275.15491	51
0.50, 0.72, 0.81	1.387	103.5	12.44	15.16	15.31	16.06	18.64	18.77	19.58	0.86	-275.39789	33
0.40, 0.72, 0.81	1.380	103.4	13.35	15.98	16.25	17.10	19.76	19.74	20.37	0.53	-275.64204	16
0.30, 0.72, 0.81	1.373	103.4	14.28	16.80	17.20	18.14	20.89	20.72	21.17	1.28	-275.88728	-1
0.40, 0.50, 0.81	1.370	103.4	13.18	15.93	16.19	17.05	19.80	19.82	20.49	0.53	-275.05476	32
0.40, 0.25, 0.81	1.359	103.2	12.98	15.87	16.13	17.00	19.86	19.92	20.62	0.55	-274.38835	50
0.40, 0.00, 0.81	1.349	103.1	12.78	15.81	16.06	16.96	19.91	20.01	20.75	0.59	-273.72293	68
0.00, 0.00, 0.81	1.328	103.1	16.46	19.14	19.88	21.14	24.40	24.02	24.04	4.08	-274.70837	3
0.40, 0.72, 1.00	1.379	103.4	13.15	15.79	16.05	16.90	19.58	19.56	20.19	0.50	-275.37420	18
0.30, 0.72, 1.00	1.373	103.4	14.07	16.61	17.00	17.94	20.70	20.54	20.99	1.11	-275.61934	1
0.30, 0.72, 0.60	1.374	103.5	14.51	17.02	17.42	18.36	21.09	20.92	21.37	1.47	-276.18348	-3
B3PW91:												
0.80, 0.72, 0.81	1.401	104.0	9.57	12.64	12.48	12.96	15.34	16.07	17.39	3.55	-274.56710	88
0.60, 0.72, 0.81	1.384	103.6	11.37	14.30	14.33	15.01	17.58	17.92	18.95	1.72	-275.05061	51
0.50, 0.72, 0.81	1.376	103.6	12.28	15.13	15.28	16.04	18.70	18.88	19.75	0.85	-275.29426	34
0.40, 0.72, 0.81	1.369	103.5	13.19	15.96	16.23	17.09	19.83	19.85	20.54	0.54	-275.53904	16
0.30, 0.72, 0.81	1.363	103.5	14.12	16.79	17.19	18.13	20.95	20.84	21.35	1.30	-275.78489	-1
0.40, 0.50, 0.81	1.360	103.4	13.02	15.90	16.17	17.04	19.87	19.93	20.66	0.55	-274.95222	32
0.40, 0.25, 0.81	1.349	103.3	12.82	15.84	16.11	17.00	19.93	20.03	20.79	0.60	-274.28631	51
0.40, 0.00, 0.81	1.340	103.2	12.62	15.78	16.04	16.95	19.98	20.12	20.91	0.67	-273.62140	70
0.00, 0.00, 0.81	1.320	103.2	16.31	19.14	19.88	21.15	24.48	24.15	24.23	4.12	-274.60899	4
0.40, 0.72, 1.00	1.366	103.5	13.06	15.88	16.15	17.01	19.78	19.82	20.53	0.52	-275.37097	19
0.30, 0.72, 1.00	1.360	103.5	13.99	16.71	17.10	18.06	20.90	20.81	21.34	1.24	-275.61689	2
0.30, 0.72, 0.60	1.367	103.5	14.26	16.88	17.28	18.22	21.00	20.87	21.36	1.36	-275.97068	-4

TABLE IV.
(Continued)

Method ^a	Distance, Å	Angle, deg.	I_i or $ \varepsilon_i $, ev								rms error, ev	E_{tot} , hartrees	$\Delta H_{\text{atomiz.}}$, kcal/mol
B3P86:													
0.80, 0.72, 0.81	1.399	103.9	10.14	13.23	13.06	13.54	15.95	16.67	18.00	2.96	−275.11862	96	
0.60, 0.72, 0.81	1.382	103.6	11.94	14.88	14.92	15.60	18.19	18.53	19.56	1.29	−275.60228	59	
0.50, 0.72, 0.81	1.374	103.5	12.85	15.71	15.86	16.63	19.31	19.49	20.35	0.43	−275.84599	41	
0.40, 0.72, 0.81	1.368	103.5	13.76	16.54	16.81	17.67	20.43	20.46	21.15	0.93	−276.09084	24	
0.30, 0.72, 0.81	1.362	103.5	14.69	17.37	17.77	18.72	21.56	21.45	21.95	1.85	−276.33674	7	
0.40, 0.50, 0.81	1.358	103.4	13.59	16.49	16.75	17.63	20.48	20.54	21.26	0.94	−275.50407	40	
0.40, 0.25, 0.81	1.348	103.3	13.39	16.43	16.69	17.58	20.53	20.63	21.39	0.96	−274.83823	59	
0.40, 0.00, 0.81	1.338	103.2	13.19	16.37	16.62	17.54	20.59	20.72	21.51	0.98	−274.17337	77	
0.00, 0.00, 0.81	1.318	103.1	16.88	19.73	20.46	21.74	25.09	24.76	24.83	4.70	−275.16114	12	
0.40, 0.72, 1.00	1.365	103.4	13.65	16.48	16.74	17.61	20.41	20.45	21.15	0.90	−275.92843	28	
0.30, 0.72, 1.00	1.359	103.4	14.58	17.31	17.70	18.66	21.53	21.43	21.95	1.80	−276.17438	11	
0.30, 0.72, 0.60	1.365	103.5	14.81	17.44	17.84	18.79	21.59	21.46	21.95	1.89	−276.51632	3	

^a All calculations were with the 6-31+G** basis set. For each functional combination, the values of A, B, and C are given to identify the parametrization. The first set (A = 0.80, B = 0.72, and C = 0.81) is the standard one.

^b Distance and angle: ref. 42; ionization potentials: ref. 40; atomization energies: ref. 41.

TABLE V.
Experimental and Computed Data for H₂O.

Method ^a	Distance, Å	Angle, deg.	I_i or $ \epsilon_i $, eV			rms error, eV	E_{tot} , hartrees	$\Delta H_{\text{atomiz.}}$, kcal/mol
Experiment ^b	0.958	104.5	12.62	14.74	18.51	—	—	221.6
Hartree–Fock	0.943	107.1	13.87	15.81	19.94	1.26	−76.03123	143
B3LYP:								
0.80, 0.72, 0.81	0.965	105.7	8.74	10.73	14.75	3.88	−76.43405	217
0.60, 0.72, 0.81	0.956	106.1	10.33	12.31	16.40	2.28	−76.59810	206
0.50, 0.72, 0.81	0.951	106.3	11.13	13.11	17.22	1.48	−76.68061	200
0.40, 0.72, 0.81	0.947	106.4	11.95	13.92	18.06	0.66	−76.76342	195
0.30, 0.72, 0.81	0.943	106.5	12.77	14.74	18.90	0.24	−76.84653	189
0.40, 0.50, 0.81	0.948	106.6	11.87	13.83	17.98	0.75	−76.57214	202
0.40, 0.25, 0.81	0.949	106.8	11.77	13.72	17.89	0.85	−76.35502	210
0.40, 0.00, 0.81	0.950	107.0	11.68	13.61	17.79	0.94	−76.13814	218
0.00, 0.00, 0.81	0.935	107.4	14.98	16.92	21.17	2.41	−76.47088	197
0.40, 0.72, 1.00	0.948	106.4	11.76	13.73	17.85	0.86	−76.66486	194
0.30, 0.72, 1.00	0.944	106.5	12.58	14.55	18.69	0.15	−76.74791	188
0.30, 0.72, 0.60	0.942	106.5	12.98	14.96	19.13	0.43	−76.95558	190
B3PW91:								
0.80, 0.72, 0.81	0.963	105.6	8.69	10.71	14.76	3.91	−76.40460	216
0.60, 0.72, 0.81	0.953	106.0	10.29	12.30	16.41	2.29	−76.56922	204
0.50, 0.72, 0.81	0.949	106.2	11.10	13.11	17.24	1.48	−76.65199	199
0.40, 0.72, 0.81	0.945	106.3	11.92	13.93	18.08	0.67	−76.73507	193
0.30, 0.72, 0.81	0.941	106.4	12.75	14.76	18.93	0.25	−76.81843	188
0.40, 0.50, 0.81	0.946	106.5	11.84	13.84	18.00	0.75	−76.54380	201
0.40, 0.25, 0.81	0.947	106.7	11.75	13.73	17.91	0.84	−76.32668	209
0.40, 0.00, 0.81	0.948	106.9	11.66	13.62	17.82	0.94	−76.10981	217
0.00, 0.00, 0.81	0.933	107.3	14.97	16.95	21.22	2.43	−76.44351	196
0.40, 0.72, 1.00	0.945	106.3	11.84	13.85	18.00	0.74	−76.67632	193
0.30, 0.72, 1.00	0.941	106.4	12.67	14.68	18.85	0.20	−76.75969	187
0.30, 0.72, 0.60	0.941	106.4	12.84	14.84	19.01	0.32	−76.88338	188
B3P86:								
0.80, 0.72, 0.81	0.963	105.7	9.26	11.28	15.32	3.34	−76.61055	224
0.60, 0.72, 0.81	0.953	106.0	10.86	12.87	16.97	1.73	−76.77521	213
0.50, 0.72, 0.81	0.949	106.2	11.67	13.68	17.81	0.92	−76.85800	208
0.40, 0.72, 0.81	0.945	106.4	12.49	14.49	18.65	0.18	−76.94109	202
0.30, 0.72, 0.81	0.941	106.5	13.32	15.32	19.49	0.77	−77.02447	197
0.40, 0.50, 0.81	0.946	106.6	12.41	14.40	18.56	0.23	−76.74983	209
0.40, 0.25, 0.81	0.947	106.8	12.32	14.29	18.47	0.31	−76.53274	217
0.40, 0.00, 0.81	0.948	107.0	12.23	14.18	18.38	0.40	−76.31589	226
0.00, 0.00, 0.81	0.933	107.4	15.54	17.51	21.78	2.99	−76.64964	205
0.40, 0.72, 1.00	0.945	106.4	12.43	14.43	18.58	0.21	−76.88420	203
0.30, 0.72, 1.00	0.941	106.5	13.25	15.26	19.42	0.71	−76.96758	197
0.30, 0.72, 0.60	0.941	106.5	13.39	15.39	19.57	0.84	−77.08738	196

^a All calculations were with the 6-31+G** basis set. For each functional combination, the values of A, B, and C are given to identify the parametrization. The first set (A = 0.80, B = 0.72, and C = 0.81) is the standard one.

^b Distance and angle: ref. 39; ionization potentials: ref. 40; atomization energies: ref. 41.

and γ) generally has only minor consequences, most notable for the N—O and F—O bonds. Particularly striking is the shortening of the latter with decreasing β (about 0.03 Å when β goes from 0.72 to 0.00). Finally, the angles in F₂O and H₂O tend to be relatively little affected by changing the α , β , γ combination. The primary exceptions to this are when $\alpha = \beta = 0$ for H₂O.

TOTAL ENERGIES AND ATOMIZATION ENTHALPIES

As expected, the standard Becke parameters give the most accurate atomization enthalpy in most instances, although the corresponding total energies are among the least negative. As α is decreased, with $\beta = 0.72$, $\gamma = 0.81$, the total energies become more negative but $\Delta H_{\text{atomiz.}}$ drops rapidly; for $\alpha = 0.40$, the changes relative to $\alpha = 0.80$ are about 39 kcal/mol for HCN and N₂, 80 for N₂O, 72 for F₂O, and 22 for H₂O. In fact, the LYP and PW91 calculations with $\alpha = 0.30$, $\beta = 0.72$, $\gamma = 0.81$ predict F₂O to be unbound! Lowering β (nonlocal exchange) makes the total energy more positive, but markedly improves the $\Delta H_{\text{atomiz.}}$. Thus, $\alpha = 0.40$, $\beta = 0.00$, $\gamma = 0.81$ yields more positive total energies than any other combination, but the atomization enthalpies are actually more accurate than for the standard parameters in three cases. Increasing and decreasing γ (nonlocal correlation) respectively raises and lowers the total energy, but has little effect upon $\Delta H_{\text{atomiz.}}$ for HCN, N₂, and H₂O; for N₂O and F₂O, the consequences for $\Delta H_{\text{atomiz.}}$ are slightly greater—3 or 4 kcal/mol. For each molecule and each functional, the parameter combination producing the most negative total energy (of those tested), but one of the least accurate $\Delta H_{\text{atomiz.}}$, was $\alpha = 0.30$, $\beta = 0.72$, $\gamma = 0.60$.

Discussion

There is no single α , β , γ combination that can be identified as the optimum one for predicting electronic ionization potentials. However the results in Tables I–V indicate that α is the most important determinant of B3 orbital energies, and that $\alpha = 0.40$ is overall the most effective of the values investigated. Thus, the rms error obtained for all five molecules with the five $\alpha = 0.40$ combinations tested in this work is about 0.74 eV. This is considerably better than the best of the Hartree–Fock (1.26 eV, for H₂O). Of course, there are some notable special cases. For example, the $\alpha = 0.30$, $\beta = 0.72$, $\gamma = 1.00$ combination produced rms errors ≤ 0.20 eV for H₂O (LYP

and PW91), and $\alpha = 0.50$, $\beta = 0.72$, $\gamma = 0.81$ gave rms errors ≤ 0.50 eV for N₂O and F₂O (P86).

Hartree–Fock orbital energies tend to give better approximations to the ionization potentials of the highest occupied orbitals than the lower ones.³⁴ For the molecules in Tables I–V, the Hartree–Fock rms error for the highest orbital is 1.38 eV compared to 2.22 overall. For the $\alpha = 0.40$ combinations, the rms error for the highest orbital is 0.71 eV.

The trends shown by the atomization enthalpies in Tables I–V are interesting and suggestive. Equation (1) contains three types of terms: local density approximations, nonlocal corrections to these, and Hartree–Fock. It is well known that local density procedures considerably overestimate binding energies.^{44–48} Becke demonstrated that the error can be substantially reduced by introducing his gradient correction;⁹ for a group of 55 molecules, the average absolute deviation dropped from 36.2 to 3.7 kcal/mol.⁴⁹ On the other hand, Hartree–Fock calculations greatly underestimate binding energies,⁴³ as is confirmed again in Tables I–V. Becke's standard α , β , γ represents an optimum balance between these various tendencies. When α is decreased (so as to increase the magnitudes of the B3 orbital energies), then the role of local exchange is diminished and that of Hartree–Fock expanded, and the atomization enthalpies consequently become smaller. This can be reversed, however, by lessening the reducing effect of Becke's nonlocal exchange correction. As β is decreased (with $\alpha = 0.40$, $\gamma = 0.81$), the $\Delta H_{\text{atomiz.}}$ increase until they are very similar to the values obtained with the standard parameters for HCN and H₂O, and approaching them for the other three molecules.

One can accordingly speculate that it may often be possible to obtain B3 $|\epsilon_i|$ that are reasonable approximations to the electronic ionization potentials while maintaining satisfactory accuracy for other properties. This might be done, for example, by setting $\alpha = 0.40$, $\beta = 0.00$. The molecules that may pose a problem, based on the data in Tables I–V, are those having several linked "electron-rich" atoms, such as N, O, and F, which have high outer-shell electron densities.⁵⁰ Computational challenges associated with such molecules have been noted earlier,^{43, 51–55} although the focus has been upon the treatment of correlation.

Conclusions

It is certainly feasible, by suitable modification of the parameters in eq. (1), to achieve $|\epsilon_i|$ that are

good approximations to the experimental electronic ionization potentials. The primary determinant is α , which governs the proportions of Slater local and Hartree–Fock exchange to be included. The parameter γ can be adjusted to further improve the agreement. The particular α , γ combination that should be selected in any given case depends upon the correlation function being used and the general class of compounds to which the molecule of interest belongs; the data in Tables I–V provide some guidelines, and additional tests could, of course, be made for specific types of molecules. In general, $\alpha = 0.40$ appears to be a good starting point.

Our results suggest that for many organic molecules and others that do not involve bonds between N, O, and/or F atoms, setting $\beta = 0.00$ in conjunction with $\alpha = 0.40$ may produce acceptable approximations to electronic ionization potentials without an undue sacrifice of accuracy in other properties. This speculation will, of course, require considerable further investigation. In those instances in which this approach is not successful (e.g., N_2O and F_2O), it may be necessary to determine ionization potentials and other properties in separate runs.

Acknowledgments

We greatly appreciate the support of Program Officer Dr. Judah Goldwasser from the Office of Naval Research.

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